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(54) Title: MESH-FORMING MATERIAL AND METHOD OF MAKING THE SAME			
(57) Abstract A method of melt grafting acrylic acid onto a polyolefin to form a modified polyolefin is disclosed. Also disclosed is a water-responsive article and a method of making the article formed from a compositional blend having from about 15 weight percent to about 50 weight percent of the modified polyolefin and from about 85 weight percent to about 50 weight percent poly(ethylene oxide).			

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5 MESH-FORMING MATERIAL AND METHOD OF MAKING THE SAME
FIELD OF THE INVENTION

10 The present invention relates to method of making a modified polyolefin and a water-responsive article made from a compositional thermoplastic blend of hydrophilic and hydrophobic polymers. More particularly, the present invention relates to a polyolefin having acrylic acid grafted thereto and a water-responsive article comprising the grafted polyolefin and poly(ethylene oxide).

BACKGROUND OF THE INVENTION

15 Personal care products, such as diapers, sanitary napkins, adult incontinence garments, and the like are generally constructed from a number of different components and materials. Such articles usually have some portion, usually the backing layer, constructed of a liquid repellent film material. The liquid repellent film commonly used includes plastic materials such as a polyethylene film or copolymers of ethylene and other polar and nonpolar monomers. The purpose of the liquid repellent layer is to minimize or prevent absorbed liquid from exuding from the absorbent which may then soil the user or adjacent clothing. The liquid repellent film also has the advantage of allowing greater utilization of the absorbent capacity of the product.

25 Although such products are relatively inexpensive, sanitary and easy to use, disposal of a soiled product is not without its problems. Typically, the soiled products are disposed in a solid waste receptacle. This adds to solid waste disposal costs and presents health risks to persons who may come in contact with the soiled product. An ideal disposal alternative would be to use municipal sewage treatment and private residential septic systems by flushing the soiled product in a toilet.

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Products suited for disposal in sewage systems are termed "flushable." While flushing such articles would be convenient, the liquid repellent material normally does not disintegrate in water. This tends to plug toilets and sewer pipes. At the municipal sewage treatment plant the liquid repellent material may disrupt operations by plugging screens and causing sewage disposal problems. It therefore becomes necessary, although undesirable, to separate the barrier film material from the absorbent article prior to flushing.

In addition to the article itself, typically the packaging in which the disposable article is distributed is also made from a water resistant material. Water resistivity is necessary to prevent the degradation of the packaging from environmental conditions and to protect the disposable articles therein. Although this packaging may be safely stored with other refuse for commercial disposal, and especially in the case of individual packaging of the products, it is often more convenient to dispose of the packaging in the toilet with the discarded disposable article. However, where such packaging is composed of a water resistant material, the aforementioned problems persist.

Over the past decade or so interest has grown in modifying existing polymers in an effort to overcome these deficiencies and to achieve commercially important copolymers having improved and, at times, specific properties. This has been particularly evident in the drive to modify commodity polymers such as polyolefins with polar functional monomers such as acrylic acid and alkyl acrylates. For example, linear low-density polyethylene has been modified by melt grafting up to about 5 weight percent (wt. %) t-butylaminoethyl methacrylate (t-BAEMA) to produce a copolymer having improved properties for co-extrusion as tie layers. These tie layers are commercially important in the packaging and film industry to economically produce packages meeting specific requirements and sometimes governmental regulations.

Polyolefins have also been modified using acrylate esters such as methyl acrylate, 2-butyl acrylate, 2-ethylhexyl acrylate, decyl acrylate, octadecyl acrylate and corresponding esters of methacrylate.

Accordingly, there is still a need for a water responsive material that would be useful in a disposable personal care product, easy to manufacture and that could be economically and efficiently produced.

SUMMARY OF THE INVENTION

One aspect of the present invention is a method of making a modified polyolefin having from about 0.5 weight percent to about 30 weight percent of acrylic acid grafted thereto, wherein the percent grafted acrylic acid is based on the total weight of the polyolefin and the weight of the acrylic acid. The method includes the steps of adding an amount of polyolefin with predetermined amounts of a free radical initiator and acrylic acid to a reaction vessel and mixing the constituents under melt grafting conditions to form the modified or grafted polyolefin. As used herein, the terms "modified polyolefin" and "grafted polyolefin" are used interchangeably. The modified polyolefin may then be formed into an article of choice using methods well known in the art or solidified and pelletized for later thermoforming operations.

Another aspect of the present invention is compositional blend having at least about 15 weight percent of the modified polyolefin and about 85 weight percent of poly(ethylene oxide).

Another aspect of the present invention is a water-responsive article, such as a film, having at least 15 weight percent of the modified polyolefin and about 85 weight percent of poly(ethylene oxide) wherein the article is mesh-forming when subjected to water immersion.

It is an object of the invention to provide a method of making a modified polyolefin. Specifically, it is an object of the invention to provide a method for grafting acrylic acid onto a polyolefin.

It is another object of the invention to provide a compositional blend having at least 15 weight percent of the modified polyolefin and about 85 weight percent of poly(ethylene oxide).

Another object of the invention is to provide a water-responsive article having at least 15 weight percent of the modified polyolefin and about 85 weight percent of poly(ethylene oxide).

It is another object of the invention to provide a water-responsive article having a modified polyethylene or modified polypropylene as a portion of its composition.

It is another object of the invention to provide a water-responsive article that will form an open pore structure when immersed in water for less than about 2 minutes.

As used herein, the term "water-responsive" includes an article that is water-dispersible and/or mesh-forming when tested in accordance with the water-responsive test described below.

"Water-dispersible" is used herein to describe a 5 mil (0.005 of an inch) film that, under the water-responsive test described below, dissolves or breaks into pieces smaller than 20 mesh.

5 "Mesh-forming" describes a 5 mil film that, under the water-responsive test, remains in tact but loses rigidity and forms an open pore structure having an average pore size of less than about 500 microns.

DETAILED DESCRIPTION OF THE INVENTION

10 One aspect of the invention provides a method for grafting acrylic acid onto a polyolefin. Broadly, the method includes the steps of blending an amount of the polyolefin with a free radical initiator and acrylic acid (collectively reactants) in a reaction vessel and mixing the reactants under melt grafting conditions to graft from about 0.5 weight percent to about 30 weight percent acrylic acid onto the polyolefin.

15 The saturated ethylene polymers useful in the practice of this invention are homopolymers or copolymers of ethylene and polypropylene and are essentially linear in structure. As used herein, the term "saturated" refers to polymers which are fully saturated, but also includes polymers containing up to about 5% unsaturation. The homopolymers of ethylene include those prepared under either low pressure,
20 i.e., linear low density or high density polyethylene, or high pressure, i.e., branched or low density polyethylene. High density polyethylenes are typically characterized by a density that is about equal to or greater than 0.94 grams per cubic centimeter (g/cc). The high density polyethylenes useful as a base resin in the present invention have a density ranging from about 0.94 g/cc to about 0.97 g/cc. The
25 polyethylenes can have a melt index, as measured at 2.16 kg and 190°C, ranging from about 0.01 decigrams per minute (dg/min) to 100 dg/min. Desirably, the polyethylene has a melt index of 0.01 dg/min to about 50 dg/min and more desirably of 0.05 dg/min to about 25 dg/min. Alternatively, mixtures of polyethylene can be used as the base resin in producing the graft copolymer compositions, and such
30 mixtures can have a melt index greater than 0.005 dg/min to less than about 100 dg/min.

The low density polyethylene has a density of less than 0.94 g/cc and are usually in the range of 0.91 g/cc to about 0.93 g/cc. The low density polyethylene has a melt index ranging from about 0.05 dg/min to about 100 dg/min and desirably
35 from 0.05 dg/min to about 20 dg/min. Ultra low density polyethylene can be used in accordance with the present invention. Generally, ultra low density polyethylene has a density of less than 0.90g/cc.

Generally, polypropylene has a semi-crystalline structure having a molecular weight of about 40,000 or more, a density of about 0.90 g/cc, a melting point of about -168°C to about 171°C for isotactic polypropylene and a tensile strength of 5000 psi. Polypropylene can also have other tacticities including syndiotactic and atactic.

The above polyolefins can also be manufactured by using the well known multiple-site Ziegler-Natta catalysts or the more recent single-site metallocene catalysts. The metallocene catalyzed polyolefins have better-controlled polymer microstructures than polyolefins manufactured using Ziegler-Natta catalysts, including narrower molecular weight distribution, well-controlled chemical composition distribution, comonomer sequence length distribution, and stereoregularity. Metallocene catalysts are known to polymerize propylene into atactic, isotactic, syndiotactic, isotactic-atactic stereoblock copolymer.

Copolymers of ethylene which can be useful in the present invention may include copolymers of ethylene with one or more additional polymerizable, unsaturated monomers. Examples of such copolymers include, but are not limited to, copolymers of ethylene and alpha olefins (such as propylene, butene, hexene or octene) including linear low density polyethylene, copolymers of ethylene and vinyl esters of linear or branched carboxylic acids having 1-24 carbon atoms such as ethylene-vinyl acetate copolymers, and copolymers of ethylene and acrylic or methacrylic esters of linear, branched or cyclic alkanols having 1-28 carbon atoms. Examples of these latter copolymers include ethylene-alkyl (meth)acrylate copolymers, such as ethylene-methyl acrylate copolymers.

The mixture of polyolefin and acrylic acid are subjected to mechanical deformation in the presence of the free radical initiator in a suitable mixing device, which preferably, is an extruder. The extruder can have more than one port for the addition of the polyolefin polymer. Desirably, there is at least one injection port on the extruder that is at a position where polyolefin is melted or at least partially melted for addition of acrylic acid and/or the initiator. The extruder may also have a section with a reduced pressure zone for venting off any unreacted acrylic acid and/or volatiles formed during the process.

Free radical initiators useful in the practice of this invention include acyl peroxides such as benzoyl peroxide; dialkyl; diaryl; or aralkyl peroxides such as di-t-butyl peroxide; dicumyl peroxide; cumyl butyl peroxide; 1,1-di-t-butyl peroxy-3,5,5-trimethylcyclohexane; 2,5-dimethyl-2,5-di(t-butylperoxy) hexane; 2,5-dimethyl-2,5-bis(t-butylperoxy) hexyne-3 and bis(a-t-butyl peroxyisopropylbenzene); peroxyesters such as t-butyl peroxyvalate; t-butyl peroctoate; t-butyl perbenzoate; 2,5-

dimethylhexyl-2,5-di(perbenzoate); t-butyl di(perphthalate); dialkyl peroxy monocarbonates and peroxydicarbonates; hydroperoxides such as t-butyl hydroperoxide, p-methane hydroperoxide, pinane hydroperoxide and cumene hydroperoxide and ketone peroxides such as cyclohexanone peroxide and methyl ethyl ketone peroxide. Azo compounds such as azobisisobutyronitrile may also be used.

Other components well known in the art can be added to the graft copolymers to further enhance the properties of the resulting material. For example, polyethylene glycol can be added to improve the melt viscosity. Additives of other types normally used in polymer blends can also be incorporated to provide specific properties as needed. For example, anti-static agents, pigments, colorants and the like. Additionally, processing characteristics can be improved by incorporating lubricants or slip agents into the blends. All of these additives are generally used in relatively small amounts, usually less than 3 weight percent.

The feed rates of the constituents to the extruder are important. The acrylic acid and initiator can be metered continuously into the extruder or in several portions over a period of time to promote homogeneous grafting of the acrylic acid throughout the mass of the melted polyolefin polymer. The free radical initiator should be fed to the melt at a rate relative to the feed rate of the acrylic acid, that is, the ratio of initiator feed (weight basis) to acrylic acid feed (weight basis) is greater than about 0.025, preferably, the free radical initiator relative feed rate is from about 0.025 to about 0.1, more preferably, from about 0.025 to about 0.075 and most preferably, from about 0.0375 to about 0.06.

Desirably, the acrylic acid monomer can be fed to the melt at a rate relative to the feed rate of the polyolefin, that is, the ratio of acrylic acid monomer (weight basis) to polyolefin (weight basis) is from 0.02 to about 0.3 preferably the monomer relative feed rate is from about 0.05 to about 0.25 and more preferably, the relative feed rate is from about 0.1 to about 0.2.

The grafted acrylic acid content of the final modified polyolefin polymer can be from about 0.5 weight percent to about 15 weight percent based on the total amount of acrylic acid and polyolefin resin fed. Desirably, the polyolefin, i.e. polyethylene or polypropylene, has grafted thereto from about 0.75 weight percent to about 10 weight percent.

Although specific values have been stated for the ranges above, one skilled in the art would understand that such ranges implicitly include all values within those ranges without specifically stating such values herein.

Another aspect of the invention is a water-responsive thermoplastic article made from a compositional blend of the modified polyolefin and poly(ethylene oxide). Suitable poly(ethylene oxide) resins can have a molecular weight ranging from about 100,000 to about 8,000,000. Poly(ethylene oxide) is available from Union Carbide Corporation under the trade name of POLYOX®. Typically, poly(ethylene oxide) is a dry free flowing white powder having a crystalline melting point in the order of about 65°C, above which the poly(ethylene oxide) resin becomes thermoplastic and can be formed by molding, extrusion and other methods known in the art. The blend has from about 15 weight percent to about 50 weight percent of the modified polyolefin and from about 85 weight percent to about 50 weight percent poly(ethylene oxide). Preferably, the blend has from about 20 weight percent to about 50 weight percent of the modified polyolefin and from about 80 weight percent to about 50 weight percent poly(ethylene oxide) and more preferably, from about 30 weight percent to about 50 weight percent of the modified polyolefin and from about 70 weight percent to about 50 weight percent poly(ethylene oxide). The article can be made by blending under melt conditions the above described portions of the above described modified polyolefin and poly(ethylene oxide) and forming the article from the melt blend.

Unexpectedly, the article formed from the blend is mesh-forming when immersed in water. A five mil thick film made from the blend will form a mesh having an average pore size, as determined by the equivalent hydraulic diameter, of less than about 500 microns. Desirably, the mesh will have an average pore size of a few micron to 200 microns and more preferably from about 40 microns to about 200 microns. Water-responsive articles that can be produced from the blends include thermoplastic tampon tubes, garbage bags, thermoplastic films and personal care barrier films. One skilled in the art would also understand that the porous mesh itself may be used as a porous membrane for filtration. To have a water response time of less than about 2 minutes, desirably, the wall thickness or caliper of the article, e.g., the tampon applicator or film is 5 mils or less. One would understand that an article having a caliper greater than 5 mils would still be water-responsive but may take longer than 2 minutes after being subjected to water before becoming affected. It is to be understood that, as for a film, "caliper" and "thickness" may be used interchangeably. However, in a shaped article, such as a tube or other configuration having a wall, the caliper of the wall would more accurately describe the thickness measurement.

Processing characteristics of the blends can be enhanced by the incorporation of lubricants or slip agents into the blends in an amount up to about 5 weight percent. A typical blend formulation including a lubricant would be in the

order of about 75 weight percent of poly(ethylene oxide), about 20 weight percent of a polyolefin and about 5 weight percent of a lubricant. Such lubricants are well known in the art and include Tween 20, Turgitol NP13 available from Union Carbide and various fatty acids such as Kenamide E available from Witco Chemical.

5 In addition, the blends may contain other components to enhance the properties of the resulting material. For example, polyethylene glycol can be added to lower the melt viscosity of the melted blend to a range suitable for other processes such as meltblown or meltsprayed nonwoven materials. The amount of polyethylene glycol can be from about 0.1 weight percent to about 10 weight percent. Suitable
10 polyethylene glycols are available from Union Carbide under the tradename CARBOWAX®.

The polyolefin and poly(ethylene oxide) blend of the invention can be prepared by mixing the desired weight ratio of the constituents into a blend using any standard equipment commonly used for blending and preferably, melt blending
15 thermoplastic resins. For example, a batch or continuous blender may be used to blend the polyolefin and poly(ethylene oxide) using heat and high shear. After melt blending, the blend can be solidified and pelletized or extruded into a film using techniques known in the art. Importantly, the water-responsive blend of the present invention is capable of being thermoformed using conventional techniques known in
20 the art.

The present invention is illustrated in greater detail by the specific examples presented below. It is to be understood that these are illustrative embodiments and are not intended to be limiting of the invention, but rather are to be construed broadly within the scope and content of the appended claims. In all the examples, a
25 relatively short but determinable water-response time was desired.

In each of the examples below, 5 mil films were prepared from the melt blends using a Carver hot press with two heated platens at a temperature of 190°C and a pressure of 15000 psi for 3 minutes.

30 Water-Response Test:

The water-responsiveness of the five (5) mil films prepared from the melt blends was determined by testing a section of the film measuring about 0.25 of an inch by about 0.5 of an inch. Using a pair of tweezers to hold the section of film, it was immersed into a scintillation vial filled with 20 milliliters of water and held for 2
35 minutes. After 2 minutes, if the section of film begin to disperse, the contents of the scintillation vial were emptied through a "20 mesh" U.S.A. Standard Testing Sieve (ASTME-11 Specification, No. 20).

In the examples the following terms are used to describe the effect of water on the section of film:

Water-dispersible: the film dissolves or breaks into pieces smaller than 20 mesh after 2 minutes.

- 5 Mesh-forming: the film will lose rigidity and form a porous structure having an average pores size less than about 500 microns.

EXAMPLE 1

A low density polyethylene polymer having a melt index of 1.9 dg/min
10 (available from Dow Chemical Company, Midland, MI) was grafted with acrylic acid (available from Aldrich Chemical Company, Milwaukee, WI) by reactive extrusion. This was a continuous process in which the grafting reaction was conducted in a 30 millimeter twin-screw extruder (Werner & Pfleiderer, ZSK-30). The extruder had a
15 total processing length of 880 millimeters, nine barrel sections and five heating zones. Barrel no. 1 was cooled by water. The heating elements for barrels 2 and 3 were coupled as Zone 1, barrels 4 and 5 were coupled as Zone 2, barrels 6 & 7 were coupled as Zone 3, barrel 9 was Zone 4 and the die was Zone 5. The polyethylene resin feed rate was 22 lb/hr, the acrylic acid monomer feed rate was 2.2 lb/hr and the
20 respective feed rate of the free radical initiator was 0.11 lb/hr. The feed to the extruder comprised adding the low density polyethylene to the extruder at the feed throat. At barrel 5, a solution of acrylic acid and initiator (2,5-dimethyl-2,5-di(t-butylperoxy) hexane, supplied by elf Atochem, 2000 Market St., Philadelphia, PA 19103-3222 under the tradename of Lupersol 101) were added to the molten
25 polyethylene. The screw speed of the extruder was 300 rpm. The polymer melt was extruded into strands and cooled in a water bath and subsequently pelletized by a strand-cut type pelletizer. The collected pellets were dried under vacuum (29 inch Hg) for 18 hours to remove water.

Purifying the modified polyolefin for determining grafted acrylic acid content

30 To remove unreacted acrylic acid and any homopolymer of acrylic acid the reaction products were purified. To purify the modified polyolefin, 5-grams of the modified polyolefin product obtained from Example 1 above was added to a round-bottom flask containing 150 milliliters of xylenes. The flask was fitted with a condenser for refluxing and stirred by a magnetic stirrer. The contents were heated
35 to 140°C to 150°C in an oil-bath and refluxed for three (3) hours. The modified polyolefin was completely dissolved in the solution. The hot xylenes solution was added, stirring continuously, to a beaker containing 800 milliliters of acetone at room

temperature. The purified precipitate was collected by vacuum filtration and washed with 100 milliliters of acetone. The purified precipitate was dried in a vacuum oven at 50°C and 25-30 inches of Hg until all solvent had been removed.

The amount of acrylic acid grafted onto the polyethylene was determined by dissolving 0.5 grams of the purified precipitate in 50 milliliters of hot xylenes. The samples were titrated, while hot, with 0.0080 N potassium hydroxide in methanol solution. The volume of potassium hydroxide consumed was then converted into weight percent of grafted acrylic acid using the formula:

$$\% \text{ grafted acrylic acid} = [(ml \text{ KOH}) \times 0.008 \times 72.06] / [\text{wt. of sample (g)} \times 10].$$

The amount of acrylic acid grafted onto the polyethylene was determined by titration to be 0.95 weight percent.

COMPARATIVE EXAMPLE A

A blend containing 4.2 grams of the modified low density polyethylene of Example 1 and 37.8 grams of poly(ethylene oxide) having a molecular weight of 200,000 g/mol (POLYOX® WSR N-80 available from Union Carbide Corp.) was prepared using a Haake Rheomix 600 twin-roller mixer, (available from Haake, 53 West Century Rd. Paramus, NJ, 07652) for 20 minutes at a screw speed of 150 rpm. After 20 minutes, the melt was removed from the mixer and cooled in air.

The film was determined to be water-dispersible. The film began to form fine pores instantaneously. The pores were transient and unstable. After 9 seconds, the film began to disperse.

COMPARATIVE EXAMPLE B

A blend containing 5.5 grams of the modified low density polyethylene of Example 1 and 36.5 grams of poly(ethylene oxide) (POLYOX® WSR N-80) was prepared using the Haake Rheomix 600 twin-roller mixer. Each zone of the Haake mixer was preheated to 180°C. The material was mixed for 20 minutes at a screw speed of 150 rpm. After 20 minutes, the melt was removed from the mixer and cooled in air.

The film was determined to be water-dispersible. The film began to form fine pores instantaneously. The pores were transient and unstable. After 22 seconds, the film began to disperse.

COMPARITIVE EXAMPLE C

This example shows the effects of aging on the stability of the mesh. The composition of Example B was stored at ambient conditions for 1 year. A compression molded film was prepared. When a piece of the film was submerged in water the film was determined to be mesh-forming.

EXAMPLE 2

A blend containing 21 grams of the modified low density polyethylene of Example 1 and 21 grams of poly(ethylene oxide) (POLYOX® WSR N-80) was prepared using the Haake Rheomix 600 twin-roller mixer. Each zone of the Haake mixer was preheated to 180°C. The material was mixed for 20 minutes at a screw speed of 150 rpm. After 20 minutes, the melt was removed from the mixer and cooled in air.

The film was determined to be mesh-forming. After 90 seconds of water immersion a stable mesh was formed. The average pore size of the mesh was determined by equivalent hydraulic diameter to be 55.8 ± 36.8 microns. The average open area of the mesh was determined by image analysis of a photograph to be 3.2 ± 1.2 %.

EXAMPLE 3

A blend containing 12.6 grams of the modified low density polyethylene of Example 1 and 29.4 grams of poly(ethylene oxide) (POLYOX® WSR N-80) was prepared using the Haake Rheomix 600 twin-roller mixer. Each zone of the Haake mixer was preheated to 180°C. The material was mixed for 20 minutes at a screw speed of 150 rpm. After 20 minutes, the melt was removed from the mixer and cooled in air.

The film was determined to be mesh-forming. After 60 seconds of water immersion a stable mesh was formed. The average pore size of the mesh was determined to be 68.7 ± 70.6 microns and the average open area in the mesh was determined by image analysis of a photograph to be 3.9 ± 3.3 %.

EXAMPLE 4

A blend containing 9.5 grams of the modified low density polyethylene of Example 1 and 32.5 grams of poly(ethylene oxide) (POLYOX® WSR N-80) was prepared using the Haake Rheomix 600 twin-roller mixer. Each zone of the Haake mixer was preheated to 180°C. The material was mixed for 20 minutes at a screw

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speed of 150 rpm. After 20 minutes, the melt was removed from the mixer and cooled in air.

5 The film was determined to be mesh-forming. After 30 seconds of water immersion a stable mesh was formed. The average pore size of the mesh was determined to be 68.7 ± 70.6 microns and the average open area in the mesh was determined by image analysis of a photograph to be 3.9 ± 3.3 %.

EXAMPLE 5

10 A blend containing 8.4 grams of the modified low density polyethylene of Example 1 and 33.6 grams of poly(ethylene oxide) (POLYOX® WSR N-80) was prepared using the Haake Rheomix 600 twin-roller mixer. Each zone of the Haake mixer was preheated to 180°C. The material was mixed for 20 minutes at a screw speed of 150 rpm. After 20 minutes, the melt was removed from the mixer and cooled in air.

15 The film was determined to be mesh-forming. After 30 seconds of water immersion a stable mesh was formed. The average pore size of the mesh was determined to be 42.6 ± 24.8 microns and the average open area in the mesh was determined by image analysis of a photograph to be 6.5 ± 4.1 %.

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EXAMPLE 6

A blend containing 6.7 grams of the modified low density polyethylene of Example 1 and 35.3 grams of poly(ethylene oxide) (POLYOX® WSR N-80) was prepared using the Haake Rheomix 600 twin-roller mixer. Each zone of the Haake mixer was preheated to 180°C. The material was mixed for 20 minutes at a screw speed of 150 rpm. After 20 minutes, the melt was removed from the mixer and cooled in air.

The film was determined to be mesh-forming.

25 While the invention has been described with reference to specific embodiments of the invention, it is to be appreciated that various substitutions, changes, omissions and modifications may be made without departing from the scope of the invention as defined by the appended claims.

30

What is claimed is:

1. A method for grafting acrylic acid onto a polyolefin comprising the steps of:
 - a) blending an amount of the polyolefin with an amount of free radical initiator and an amount of acrylic acid in a reaction vessel; and
 - 5 b) mixing the constituents of (a) under melt grafting conditions to graft from about 0.5 weight percent to about 15 weight percent acrylic acid onto the polyolefin
2. The method of claim 1 wherein said polyolefin is polyethylene or polypropylene.
3. The method of claim 1 wherein said free radical initiator is selected from the group consisting of benzoyl peroxide; di-t-butyl peroxide; dicumyl peroxide; cumyl butyl peroxide; 1,1-di-t-butyl peroxy-3,5,5-trimethylcyclohexane; 2,5-dimethyl-2,5-di(t-butylperoxy) hexane; 2,5-dimethyl-2,5-bis (t-butylperoxy) hexyne-3;
5 bis(a-t-butyl peroxyisopropylbenzene); t-butyl peroxyisovalate; t-butyl peroctoate; t-butyl perbenzoate; 2,5-dimethylhexyl-2,5-di(perbenzoate); t-butyl di(perphthalate); t-butyl hydroperoxide; p-methane hydroperoxide; pinane hydroperoxide; cumene hydroperoxide; cyclohexanone peroxide and methyl ethyl ketone peroxide.
4. The method of claim 3 wherein the amount of acrylic acid added to the melt is about 2 weight percent to about 30 weight percent based on the amount of polyolefin.
5. The method of claim 3 wherein the amount of free radial initiator added to the melt blend is about 5 weight percent to about 25 weight percent based on the amount of acrylic acid.
6. A polyolefin having acrylic acid grafted thereto made by the process of mixing under reactive melt conditions an amount of polyolefin with an amount of free radical initiator and an amount of acrylic acid wherein from about 0.5 weight percent to about 15 weight percent acrylic acid is grafted onto said polyolefin.
7. A composition of matter comprising a blend of about 15 weight percent to about 50 weight percent of the grafted polyolefin of claim 6 and from about 85 weight percent to about 50 weight percent of poly(ethylene oxide).

8. The composition of claim 7 comprising from about 20 weight percent to about 50 weight percent of the grafted polyolefin and from about 80 weight percent to about 50 weight percent of poly(ethylene oxide).

9. The composition of claim 7 comprising from about 30 weight percent to about 50 weight percent of the grafted polyolefin and from about 70 weight percent to about 50 weight percent of poly(ethylene oxide).

10. The composition of claim 6 wherein said polyolefin is polyethylene or polypropylene.

11. The composition of claim 7 wherein said grafted polyolefin has from about 0.75 weight percent to about 10 weight percent of acrylic acid grafted thereto.

12. A water-responsive article comprising from about 15 weight percent to about 50 weight percent of the grafted polyolefin of claim 10 and from about 85 weight percent to about 50 weight percent of poly(ethylene oxide).

13. The water-responsive article of claim 12 comprising from about 20 weight percent to about 50 weight percent of the grafted polyolefin and from about 80 weight percent to about 50 weight percent of poly(ethylene oxide).

14. The water-responsive article of claim 12 comprising from about 30 weight percent to about 50 weight percent of the grafted polyolefin and from about 70 weight percent to about 50 weight percent of poly(ethylene oxide).

15. The water-responsive article of claim 12 wherein said article is a film which forms a mesh when immersed in water for two minutes.

16. The water-responsive article of claim 15 wherein said mesh has an average open pore size of less than about 500 microns.

17. The water-responsive article of claim 16 wherein said mesh has an average open pore size of about 2 microns to about 200 microns.

18. The water-responsive article of claim 16 wherein said mesh has an average open pore size of about 40 microns to about 200 microns.

19. A method of making a water-responsive article comprising the steps of:

- 5 a) blending under melt conditions from about 15 weight percent to about 50 weight percent of an acrylic acid grafted polyolefin and from about 85 weight percent to about 50 weight percent of poly(ethylene oxide) wherein said grafted polyolefin has from about 0.5 weight percent to about 15 weight percent acrylic acid grafted onto the polyolefin; and
- b) forming said article from said melt blend.

20. The method of claim 19 wherein said melt blend comprises from about 20 weight percent to about 50 weight percent of the grafted polyolefin and from about 80 weight percent to about 50 weight percent of poly(ethylene oxide).

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 97/22544

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C08F 255/02, C08L 71/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3830888 A (LAURENCE F. KING), 20 August 1974 (20.08.74), column 2, line 4 - line 9; column 4, line 50 - line 62; column 7, line 40 - line 56 --	1-6
X	EP 0725090 A2 (PCD-POLYMERE GESELLSCHAFT M.B.H.), 7 August 1996 (07.08.96), claims 1-4 --	1-6
X	US 3953655 A (ROBERT A. STEINKAMP ET AL), 27 April 1976 (27.04.76), column 4, line 12 - line 19, claim 5, ex. 1 --	1-6

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:

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Date of the actual completion of the international search

15 April 1998

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>WO 9620831 A1 (KIMBERLY-CLARK CORPORATION), 11 July 1996 (11.07.96), page 4, line 30 - page 5, line 2, claims 1,5, ex. 1</p> <p style="text-align: center;">-- -----</p> <p style="text-align: center;">Best Available Copy</p>	7-20

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INTERNATIONAL SEARCH REPORT
Information on patent family members

02/04/98

International application No.

PCT/US 97/22544

Patent document cited in search report			Publication date	Patent family member(s)		Publication date
US	3830888	A	20/08/74	BE	797691 A	03/10/73
				CA	994492 A	03/08/76
				DE	2316207 A	18/10/73
				FR	2179010 A	16/11/73
				GB	1429883 A	31/03/76
				JP	49009555 A	28/01/74
<hr/>						
EP	0725090	A2	07/08/96	DE	19500426 C	21/03/96
<hr/>						
US	3953655	A	27/04/76	US	3862265 A	21/01/75
				US	4001172 A	04/01/77
<hr/>						
WO	9620831	A1	11/07/96	AU	4643196 A	24/07/96
				CA	2209159 A	11/07/96
				EP	0800455 A	15/10/97
				PL	321539 A	08/12/97

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